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PEROXIDES OF THE ALKALINE EARTHS

First Communication

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ABSTRACT: Alkaline earth peroxides are prepared by oxidation of the hydroxide with hydrogen peroxide. Depending on the conditions, pure peroxides, their hydrates or peroxyhydrates were produced. This paper is a study of the stability of these compounds.

The alkaline earth peroxides can be prepared either by oxidation of the hydroxide with hydrogen peroxide or by addition of molecular oxygen to the oxide. In this report we concern ourselves only with the first method of preparation. It is known that depending upon the experimental conditions, pure peroxides, their hydrates or peroxyhydrates² result. The stability of these compounds has not been investigated thus far, and the delineation of this in broad outlines is the objective of the present paper. /405¹

Barium peroxide was obtained heretofore from aqueous solution only as octahydrate $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$, as decahydrate $\text{BaO}_2 \cdot 10\text{H}_2\text{O}$ or as monoperoxyhydrate $\text{BaO} \cdot \text{H}_2\text{O}_2$ [1]. A followup study showed that the decahydrate described by Berthelot [2], the existence of which had already been doubted by Schöne [3], could not be prepared [4]. Similarly, it was not possible to isolate anhydrous peroxide BaO_2 directly by precipitation from an aqueous solution. On the other hand, a heretofore undescribed diperoxyhydrate $\text{BaO}_2 \cdot 2\text{H}_2\text{O}_2$ could be produced, and it

¹ Numbers in the margin indicate pagination in the foreign text.

² As the peroxyhydrate of a material hereafter, its compound with hydrogen peroxide of crystallization will be meant.

was worthwhile on this account to investigate the conditions under which the octahydrate, the diperoxyhydrate and the monoperoxyhydrate occur and change from one to the other.

The octahydrate is always formed if a barium hydroxide solution is mixed with hydrogen peroxide and care is taken that not more than one mole barium hydroxide per mole hydrogen peroxide is present in the solution. It is also formed if the solution of any barium salt is mixed with sodium peroxide. /406

Examples: 100 cc of a saturated barium hydroxide solution was mixed with 5 cc 3% hydrogen peroxide. A silk-sheened white precipitate appeared.

Analysis:

0.2101 g substance = 0.1609 g BaSO_4 = 50.31% BaO.

0.1746 g substance = 10.8 cc 0.108-n. $\text{Na}_2\text{S}_2\text{O}_2$ = 5.35% O_2 .

From the difference: 44.34% H_2O .

BaO: act. $\text{O}:\text{H}_2\text{O}$ calculated 1 : 1 : 8
found 1.00:1.12:7.51.

1.5 g barium nitrate was dissolved in 12 cc water. To this there was added 1.4 g sodium peroxide-octahydrate in 20 cc water. A white crystalline precipitate appeared.

Analysis:

0.2007 g substance = 0.1497 g BaSO_4 = 49.00% BaO.

0.1959 g substance = 11.85 cc 0.108 n. $\text{Na}_2\text{S}_2\text{O}_3$ = 5.23% O_2 .

From the difference: 45.77% H_2O .

BaO: act. $\text{O}:\text{H}_2\text{O}$ calculated 1 : 1 : 8
found 1.00:1.02:7.96.

The diperoxyhydrate occurs if the solution of any barium salt, cooled by running water or ice, is mixed with hydrogen peroxide and precipitated with ammonia.

Example: 10 g barium chloride is dissolved in 50 cc water and mixed with a mixture of 100 cc 3% hydrogen peroxide and 10 cc 25% ammonia. Small white crystals are produced.

Analysis:

0.2616 g substance = 0.2569 g BaSO_4 = 64.52% BaO.

0.2113 g substance = 49.3 cc 0.1081 n. $\text{Na}_2\text{S}_2\text{O}_3$ = 20.18% O_2 .

From the difference: 15.30% H_2O .

BaO: act. $\text{O}:\text{H}_2\text{O}$ calculated 1 : 3 : 2
found 1.00:3.00:2.02.

If the experiment is conducted under otherwise identical conditions but at temperatures above 30°, the monoperoxyhydrate is produced.

Example: Mixture proportions as above, temperature 50°: the crystals show a trace of yellow.

Analysis:

0.2493 g substance = 0.2784 g BaSO₄ = 73.37% BaO.

0.0967 g substance = 17.08 cc 0.1081 n. Na₂S₂O₃ = 15.28% O₂.

From the difference: 11.35% H₂O.

BaO: act. O:H₂O calculated 1 : 2 : 1
found 1.00:2.00:1.32.

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At temperatures from about 100° there is no precipitate. Upon cooling, however, the octahydrate is precipitated.

Example: Mixture proportions as above, temperature about 100°. After cooling, there is a white silky sheened precipitate.

Analysis:

0.2123 g substance = 0.1593 g BaSO₄ = 49.30% BaO.

0.1296 g substance = 8.02 cc 0.1081 n. Na₂S₂O₃ = 5.35% O₂.

From the difference: 45.35% H₂O.

BaO: act. O:H₂O calculated 1:1 : 8
found 1:1.04:7.84.

While the diperoxyhydrate can thus be converted into the octahydrate by heating in aqueous solution, by action of hydrogen peroxide at low temperature the diperoxyhydrate is reformed from the octahydrate.

Example: 0.5 g barium peroxide-octahydrate is mixed with 10 cc 30% hydrogen peroxide and allowed to stand 17 hours in a closed Erlenmeyer flask with ice-salt cooling (at -3°).

Analysis:

0.1744 g substance = 0.1728 g BaSO₄ = 65.10% BaO.

0.1602 g substance = 39.0 cc 0.1081 n. Na₂S₂O₃ = 21.05% O₂.

From the difference: 13.85% H₂O.

BaO: act. O:H₂O calculated 1 : 3 : 2
found 1.00:3.10:1.81.

Only the pure octahydrate SrO₂·8H₂O has previously been prepared from the peroxides of strontium. This can be obtained through the action of hydrogen peroxide or sodium peroxide in a solution of strontium hydroxide or by mixing

Example: 1 g strontium peroxide-octahydrate is heated for 5 hours to 280°. A white powder remains.

Analysis:

0.1816 g substance = 0.2726 g SrSO_4 = 84.68% SrO .

0.1289 g substance = 18.60 cc 0.0966 n. $\text{Na}_2\text{S}_2\text{O}_3$ = 11.15% O_2 .

From the difference: 4.17% H_2O .

SrO : act. $\text{O}:\text{H}_2\text{O}$ calculated 1:1 :0
found 1:0.85:0.28.

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Of calcium only the peroxide-dihydrate $\text{CaO}_2 \cdot 2\text{H}_2\text{O}$ [5] and the peroxide-octahydrate $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ had hitherto been prepared pure in aqueous solution. It is true that Schöne [6] believed that he had also prepared a peroxide-monoperoxyhydrate $\text{CaO}_2 \cdot \text{H}_2\text{O}_2$ as a yellow powder mixed with crystals of the oxyhydrate. He did not analyze the mixture. According to our experiments, described below, it has been ascertained that Schöne had in hand a mixture of the octahydrate with anhydrous peroxide. De Forcrand [7] infers the existence of a monoperoxyhydrate from the enthalpy curves arising from the mixing of calcium hydroxide with varying amounts of hydrogen peroxide. He too was unable to isolate the monoperoxyhydrate, however.

The experiments that we undertook show that in addition to the di- and octahydrate, as with strontium, the anhydrous peroxide CaO_2 and diperoxyhydrate $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ can be obtained. And indeed the octahydrate is formed when calcium salt solutions are mixed with hydrogen peroxide and ammonia in dilute solutions even at room temperature, but in concentrated solutions only at very low temperatures. Above these temperatures, anhydrous peroxide is formed.

Examples: 11 g crystallized calcium chloride is dissolved in 5 cc water and mixed with 50 cc 3% hydrogen peroxide solution. To this solution is added, at the temperatures indicated in the first column of the following table, a solution of 7 cc 25% ammonia in 100 cc water. The second column indicates the composition of the resulting product.

Temperature	Product
-3°	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$
+8°	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$
+19°	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$
+31°	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$
+41°	Mixture
+60°	CaO_2

If under the same conditions 7 cc 25% ammonia dissolved in only 30 cc water is added, the following products result:

Temperature	Product
- 3°	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$
+ 2°	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$
+ 8°	CaO_2
+ 19°	CaO_2
+ 41°	CaO_2
+ 62°	CaO_2

The white crystalline powder of the octahydrate obtained at 8° from the dilute solution showed the following composition:

Analysis:

0.3166 g substance = 0.0854 g CaO = 26.97% CaO.

0.2124 g substance = 20.7 cc 0.0953 n. KMnO_4 = 7.43% O_2 .

From the difference: 65.60% H_2O .

CaO: act. $\text{O}:\text{H}_2\text{O}$ calculated 1:1 :8
found 1:0.97:7.57.

The anhydrous peroxide obtained at 19° from a concentrated solution as a very fine yellowish powder showed the following:

Analysis:

0.8432 g substance = 0.6178 g CaO = 73.27% CaO.

0.1435 g substance upon mixing with dilute HCl 1.50 cc O_2 (18° 745 mm Hg) = 1.35% O_2 . The solution consumes 36.58 cc 0.0853 n. $\text{Na}_2\text{S}_2\text{O}_3$ = 17.74% O_2 .

From the difference: 7.64% O_2 .

Ca: 0 : act. H_2O calculated 1:1 :0
found 1:0.91:0.32

The dihydrate as we know is obtained by introduction of the anhydrous peroxide into water. As the above experiments show, it could not be recovered by direct precipitation, because above the temperature at which the octahydrate is stable the anhydrous peroxide will soon be formed.

The diperoxyhydrate of the calcium peroxide is like that of strontium formed by the action of hydrogen peroxide on the octahydrate. It is easier than the latter to obtain in pure form.

Example: 15 cc 30% hydrogen peroxide is poured over 0.5 g calcium peroxide-octahydrate and this is allowed to stand for 70 hours in an ice-salt mixture (at 4-6°) in a closed Erlenmeyer flask. A coarse yellow powder results.

Analysis:

0.2462 g substance = 0.2441 g CaSO_4 = 40.84% CaO.

0.1271 g substance = 48.45 cc 0.1081 n. $\text{Na}_2\text{S}_2\text{O}_3$ = 32.96% O_2 .

From the difference: 26.20% H₂O.

CaO: 0: act. H₂O calculated 1 :3 :2
found 1.00:2.83:2.00.

Upon heating the octahydrate gives off its water and is converted into the anhydrous peroxide. Here it is observed that the white crystals at temperatures up to about 100° take on a yellow coloration and then on cooling retain this color permanently. With heating to about 170° a general color change from yellow to white takes place. Such white products cannot be changed back to yellow in any way. The chemical composition of both products is practically the same. The yellow form must therefore be regarded as the unstable form of calcium peroxide and the white as the stable form. The apparent contradiction implied in that some authors describe calcium peroxide as a yellow powder while others describe it as a white powder is therefore explained, in that it occurs in two different modifications. /411

Example: 1 g calcium peroxide octahydrate is heated for 5 hours to 90°. A yellow powder results.

Analysis:

0.4043 g substance = 0.3058 g CaO = 75.64% CaO.

0.1292 g substance upon mixing with dilute HCl = 1.89 cc O₂ (19°, 752 mm Hg) = 1.89% O₂. The solution consumes 33.45 cc 0.0853 n. Na₂S₂O₃ = 17.66% O₂.

From the difference: 4.81% H₂O.

Ca: 0 : act. H₂O calculated 1:1 :0
found 1:0.91:0.20

The same substance is heated for another 5 hours to 195°. It becomes pure white.

Analysis:

0.3397 g substance = 0.2582 g CaO = 76.01% CaO.

0.0810 g substance upon mixing with dilute HCl = 0.95 cc O₂ (18°, 750 mm Hg) = 1.52% O₂. The solution consumes 21.34 cc 0.0853 n. Na₂S₂O₃ = 17.97% O₂.

From the difference: 4.50% H₂O.

Ca: 0 : act. H₂O calculated 1:1 :0
found 1:0.90:0.18.

Summary

The peroxides of the three alkaline earths, barium, strontium and calcium, can be obtained in aqueous solution in three forms, namely as anhydrous peroxide, with 8 molecules water of crystallization (octahydrate) and with 2 molecules of water of crystallization (diperoxy hydrate). Barium peroxide, as was already known, also forms a compound with 1 molecule water of

crystallization (monoperoxyhydrate) and calcium peroxide, as already known, forms a dihydrate. About the formation of these products and their conversion into one another the following can be stated:

1. While anhydrous barium peroxide cannot be obtained by direct precipitation in aqueous solution, because at near 100° octahydrate is formed, it is possible in very concentrated solutions at 50° to precipitate strontium peroxide directly. Anhydrous calcium peroxide likewise is formed in dilute solutions only at higher temperatures (above 40°) but in concentrated solution it is formed even at a few degrees above 0°. /412

2. The octahydrate of barium peroxide is formed at room temperature only in strongly alkaline solutions and when an excess of hydrogen peroxide is avoided, as otherwise the diperoxyhydrate is formed. But at temperatures above 60° it is precipitated from all barium salt solutions containing hydrogen peroxide. The octahydrate of strontium peroxide is always formed when a strontium salt solution containing hydrogen peroxide is mixed with alkali, with the sole exception of extremely concentrated solutions and high temperatures, where anhydrous peroxide is formed. In the case of calcium peroxide, the octahydrate is always precipitated when the solution is so dilute and the temperature so low that the anhydrous peroxide is not yet formed.

3. In the case of barium peroxide, the diperoxyhydrate is obtained from all weakly alkaline solutions containing hydrogen peroxide under 40°. With strontium and calcium peroxide, the diperoxyhydrates cannot be obtained by direct precipitation, but they are formed only by the action of concentrated hydrogen peroxide on the octahydrates at low temperature.

4. The monoperoxyhydrate is known only for barium peroxide and in the case of this element it is only formed in the temperature range between 30° and 60°. At lower temperatures the diperoxyhydrate is formed, and at higher temperatures, the octahydrate.

5. The dihydrate, known only for calcium peroxide, cannot be obtained directly from an aqueous solution, but only indirectly via the anhydrous peroxide.

6. All peroxyhydrates of the alkaline earth peroxides in aqueous solution are converted into the octahydrates by gradual decomposition, slowly at room temperature, more rapidly at higher temperatures. All hydrates are converted into the anhydrous peroxide by cautious drying.

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